



## Produced Water Treatment Using a New Designed Electroflotation Cell

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### ABSTRACT

A novel continuous electroflotation cell, about 0.6 liter volume capacity, using aluminum electrodes was designed for oil produced water treatment. The treating performance of a novel continuous electroflotation cell for oil produced water was investigated. The pH, current density, and feed water flow rate as affecting parameters of electroflotation process were studied. The results show that the removal efficiency decreased with increasing feed flow rate. However, it increased with increasing current density. The AC current was preferred because DC current causes passivation of the anode with time. The maximum removal for all types of pollutants is achieved at pH6. The designed electroflotation cell could remove different constituents of oil produced water with range 87.5 - 99.5 % at 25°C, 5V, pH7 and AC current density of 80A/m<sup>2</sup> through a bipolar connection of the 8 electrodes with feed water flow rate of 60ml/min (3.6l/hr). The energy consumption was about 1.38Kwh/m<sup>3</sup> and the operating cost (cost/m<sup>3</sup>) was about 0.3US\$/m<sup>3</sup> for the produced water treatment.

**Keywords:** Electroflotation, produced water, water treatment, cell design.

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## 1. Introduction

The oil and gas industry produces approximately 14 billion barrels (2.2 billion cubic meters) of water annually during oil or gas extraction operations [1]. The trapped water is brought to the surface along with oil or gas is known as produced water. The produced water varies in quality and quantity so, it is considered a waste, but the industry is beginning to consider this material as a potential profit stream. Produced water must be environmentally protective or the operator could face regulatory action [2]. Produced water handling methodology depends on the composition of produced water, location, quantity and the availability of resources. Some of the options available to the oil and gas operator for managing produced water might include the treatment to meet onshore or offshore discharge regulations or to meet the quality required to use it for drilling, stimulation, and work over operations [3]. In some cases, significant treatment of produced water is required to meet the quality required for beneficial uses such as irrigation,

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rangeland restoration, cattle and animal consumption, and drinking water for private use or in public water systems [4].

Studies conducted to identify, verify, and compile existing and newly developed techniques demonstrate the economical benefits of produced water treatment. Treated produced water has the potential to be a valuable product rather than a waste. This water contains free and dispersed oil and grease with dissolved organics and salts, such as sulfates, nitrates and scaling agents, bacteria, microorganisms, algae, suspended particles, sand, turbidity, light hydrocarbon gases, carbon dioxide, hydrogen sulfide, etc. [5].

Electroflotation is a technology that combines the functions and advantages of conventional coagulation, flotation, and electrochemistry in wastewater treatment. Electroflotation was not found to be widely feasible for water treatment due to the high electricity and investment costs. Electroflotation has many benefits as compatibility, amenability to automation, cost effectiveness, energy efficiency, safety, and versatility [6]. The electroflotation process operates on the base of the principle that the cations produced electrically from iron or aluminum anodes which is responsible for the coagulation of contaminants from an aqueous medium [7]. The flocculated particles attract by small bubbles of oxygen and hydrogen generated from electrolysis of water. Thus, the flocculated particles float towards the surface [8]. One of the most important parameters that can affect the electrochemical process is current density. Current is directly proportional to the rate of electrochemical reactions. The current not only determines the coagulant dosage rate but also the bubble production rate [9]. Chloride induces breakdown of the passive layer and pitting corrosion. It reduces the adverse effect of other anions, such as sulfate and carbonate [10]. The stirring, temperature, and electrode's number and inter-distance and connection mode are important parameters that can affect the electrochemical process and energy consumption [11].

This paper aims to investigate and optimize the affecting parameters of a new designed continuous electroflotation cell for oil produced water treatment from different sources.

## **2. Materials and Methods**

### ***2.1. Produced Water Samples***

The produced water sample was collected from four oil fields to represent the average constituents of produced water from different localities.

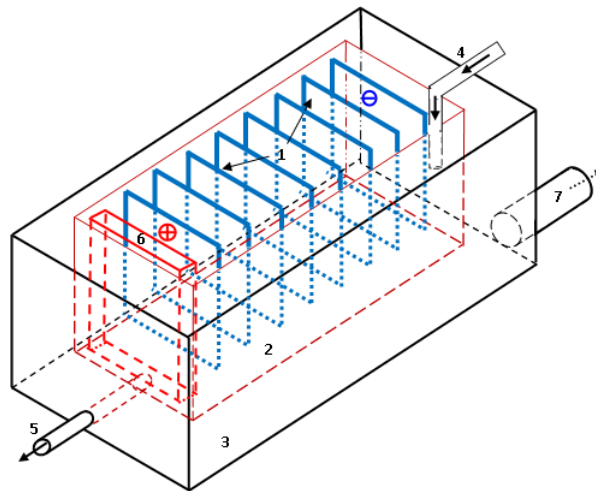
### ***2.2. Designed Cell***

The designed electroflotation cell Figures (1-4) composed of four pairs of commercially aluminum plates of 6 cm × 5 cm × 0.15 cm dimension. The inter-electrode distance between each two plates is 2cm. The aluminum plates were connected as a bipolar as shown in Figure 3. In the

bipolar connection, the two parallel electrodes that are connected to the electric power source are situated on either side of the sacrificial electrode with no electrical connection to the sacrificial electrode. Thus, during the electrolysis, the positive side undergoes an anodic reaction, whereas a cathodic reaction takes place on the negative side. The aluminum plates were placed in a plastic box of length 19.2cm, width 5.2cm and height 6.5cm (600 ml volume capacity) which was placed in a bigger one of dimension 22cm × 8cm × 7cm to collect floated flocs. The electroflotation process was carried out at 25°C, 5V and current density 80A/m<sup>2</sup> (current intensity = 1A). The feed water flow rate was varied from 20 to 80ml/min.

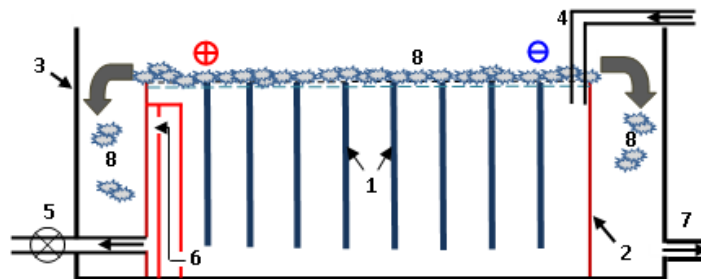
### 2.3. Characterization of Produced Water

The raw and treated produced water samples were evaluated by determining total suspended solid (TSS) according to Standard Methods [12]. The Total Organic Carbon (TOC) was determined by the UV-Persulfate TOC analyzer, model 8000 [13]. The Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD) and Total Dissolved Solid (TDS) were determined. Alkalinity is measured by neutralize the water with acid to the equivalence point [14, 15]. It was given in parts per million of equivalent calcium carbonate (ppm CaCO<sub>3</sub>). In addition, turbidity was recorded on a 2100N IS Turbidity meter (Hatch).



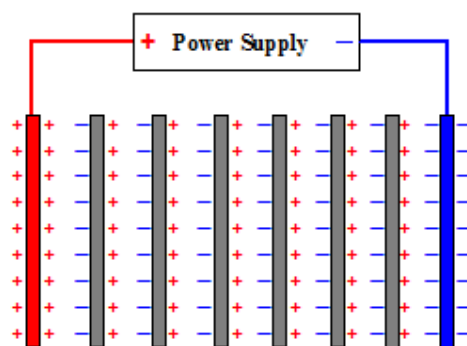
**Figure 1.** Schematic diagram of designed electroflotation cell.

(1: Aluminum plates, 2: Cell, 3: Collecting box, 4: Water inlet, 5: Water outlet, 6: Flocs trap and 7: Flocs outlet).

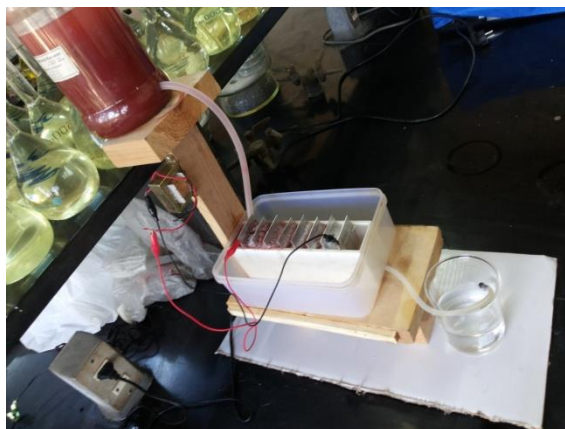


**Figure 2.** Cross section of designed electroflotation reactor.

(1: Al- plates, 2: Cell, 3: Collecting box, 4: Water inlet, 5: Water outlet, 6: Flocs trap, 7: Flocs outlet & 8: Flocs).



**Figure 3.** Electrode's polarity in a bipolar system.



**Figure 4.** Photo of the designed Electro-Flotation cell.

### 3. Results and Discussion

Through our previous research, we found that the metal ions and dyes removals by electroflotation follow pseudo first-order kinetics. The enthalpy changes ( $\Delta H^\circ$ ) were negative which suggested that the reactions are exothermic. In addition, the Gibbs free energy change ( $\Delta G^\circ$ ) was negative indicating that the removal process is spontaneous which increased with increasing temperature. Thus, the process becomes less favorable at high temperatures. Freundlich isotherm

model indicates that the metal ions removal is a heterogeneous system, which is characterized by physical adsorption. While the removal of dyes follows both Freundlich and Langmuir isotherm models which indicate that the adsorption is characterized by physical and chemical adsorptions [16, 17].

### 3.1. Effect of pH

The pH is an important factor for the removal efficiency of different pollutants. Figures 5 and 6 show the maximum removal for all types of pollutants is achieved at pH6. The removal efficiency remains high up to pH7 then it sharply increased.

The removal mechanism of pollutants is based on their adsorption on the  $\text{Al}(\text{OH})_3$  flocs. Figure 7 shows the pH affects  $\text{Al}(\text{OH})_3$  stability in the solution [18]. It demonstrates different forms of  $\text{Al}(\text{OH})_3$  relative to the pH and concentration of  $\text{Al}^{3+}$  ions in the media [19]. In the high and low pH,  $\text{Al}(\text{OH})_3$  is in its charged form and is soluble in water, hence, cannot be used for electroflotation. But in neutral pH,  $\text{Al}(\text{OH})_3$  is stable and insoluble in the water and available for pollutant adsorption from water [18].

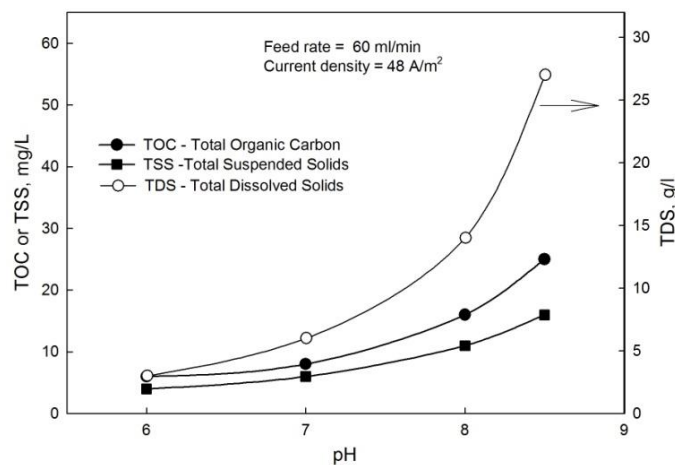
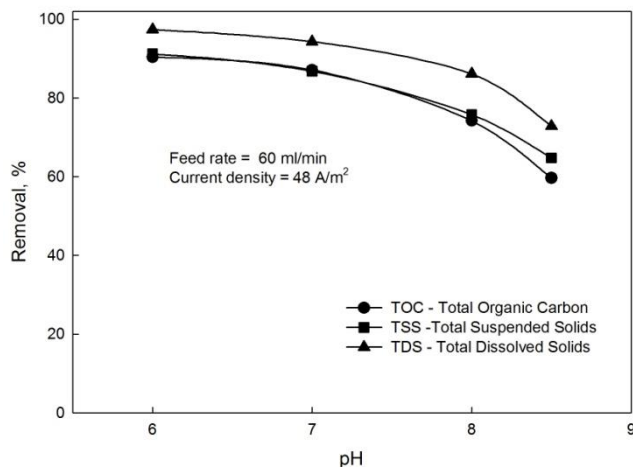


Figure 5. Effect of pH on residual constituents.

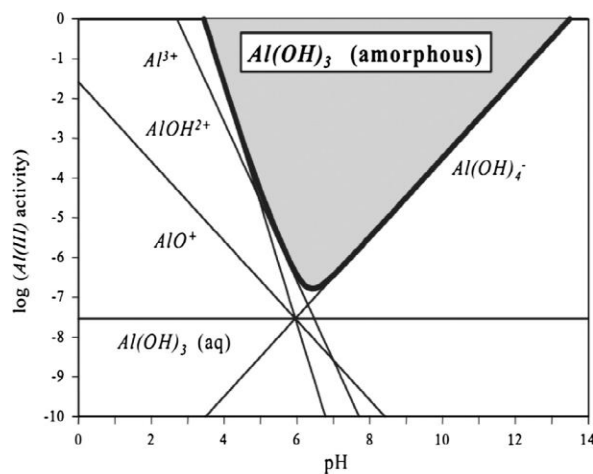
### 3.2. Effect of Current Density

The effect of current density on the treatment process is shown in Figures 8 and 9. The removal efficiency increased from about 38% to more than 96% with increasing current density from 16 to 80A/m<sup>2</sup>, at pH7 with a feed flow rate of 60ml/min. This may be due to increasing the rate of electrochemical reactions with increasing current density. The coagulant concentration produced by electrolysis on anode is typically directly proportional to the electric charge added per volume [20]. The increase in removal efficiency could be explained by greater percentage of destabilized pollutant species as a result of charge neutralization with more aluminum species released from the electrodes with increasing current density and formation of low density flocs with the more

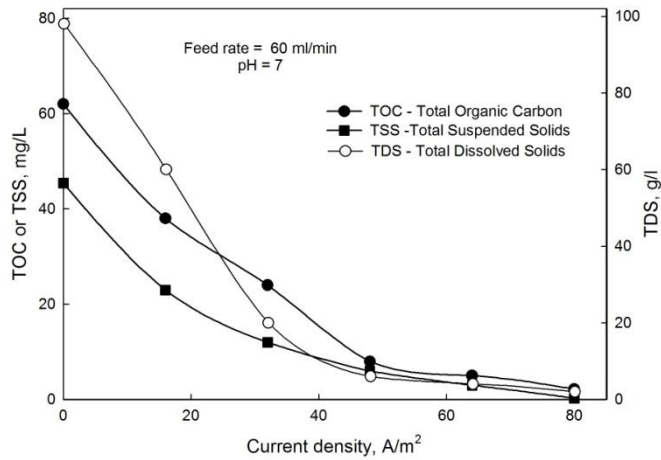
aluminum hydroxide. The current not only determines the coagulant dosage rate but also the bubble production rate [21]. The bubble size distribution is a function of the current density for a given electrode [22]. Increasing the current density decreases the bubble diameter [23]. Small bubbles have a higher probability of providing a smaller contact angle, which produces more stable aggregates [22]. Furthermore, the detention time of small bubbles in the flotation unit is longer than that of larger bubbles as they have a lower rising velocity. This promotes the probability of collision between gas bubbles and flocs [25].



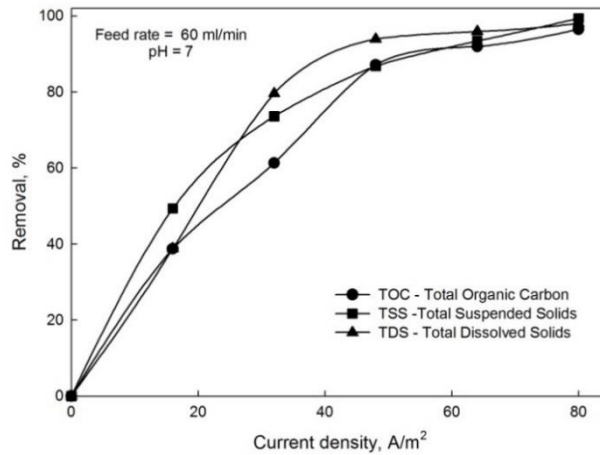
**Figure 6.** Effect of pH on removal efficiency.



**Figure 7.** Activity-pH diagram for  $\text{Al}^{3+}$  species with  $\text{Al}(\text{OH})_3$ .



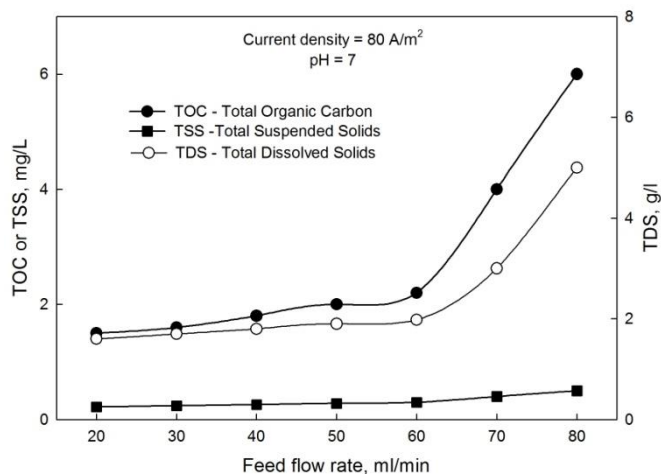
**Figure 8.** Effect of current density on residual constituents.



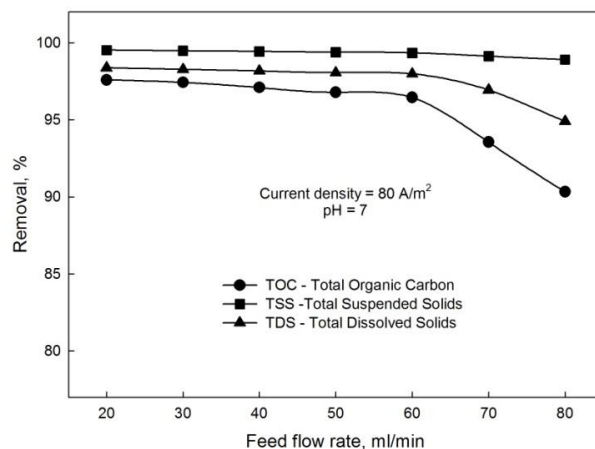
**Figure 9.** Effect of current density on removal efficiency.

### 3.3. Effect of Produced Water Flow Rate

The effect of the feed flow rate was investigated at pH7 with current density of 80A/m<sup>2</sup> (1 Ampere). Figures 10 and 11 show that the removal efficiency was slightly decreased with increasing feed flow rate up to 60ml/min (3.6L/hr) and then it was sharply decreased to 90% with increasing feed flow rate up to 80ml/min (4.8L/hr). It is important to note that, the energy consumption was increased with decreasing feed flow rate.



**Figure 10.** Effect of feed flow rate on residual constituents.



**Figure 11.** Effect of feed flow rate on removal efficiency.

Table 1 presents the analysis of produced water before and after treatment at pH7, feed flow rate of 60ml/min (3.6l/hr), current density of 80A/m<sup>2</sup> (1Ampere) and Voltage 5 at 25°C. The removal efficiency of different constituents was range between 87.5 – 99.5%.

Table 2 presents the chemical analysis of produced flocs after drying at 110°C for 2hrs. It is mainly composed of halite (NaCl), 91.22%. In addition, it also contains a relative small amount (2.6%) of aluminum hydroxide, Al(OH)<sub>3</sub>, as a result of aluminum sacrificial electrode dissolution. The remainder of about 6% was composed of NaCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> salts.



**Table 1.** Evaluation of raw and treated produced water.

| Constituents | Before (ppm) | After (ppm) | Removal (%) |
|--------------|--------------|-------------|-------------|
| TOC          | 62           | 1.5         | 97.6        |
| Hydrocarbons | 238          | 3.2         | 98.7        |
| Oil & Grease | 351          | 3.1         | 99.1        |
| COD          | 24800        | 3100        | 87.5        |
| TSS          | 45.4         | 0.22        | 99.5        |
| TDS          | 98000        | 5684        | 94.2        |
| pH           | 8.5          | 7.4         | ---         |
| Alkalinity   | 756          | 89          | 88.2        |
| Salinity     | 87000        | 5013        | 94.2        |

**Table 2.** Chemical analysis of electro-floated flocs.

| Constituent | KCl  | NaCl  | MgCl <sub>2</sub> | CaCl <sub>2</sub> | Al(OH) <sub>3</sub> | Total       |
|-------------|------|-------|-------------------|-------------------|---------------------|-------------|
| %           | 1.46 | 91.22 | 2.17              | 2.35              | 2.60                | <b>99.8</b> |

The costs involved in EF process include the cost of energy consumption, cost of dissolved electrode, and cost of external chemical (for increasing the solution conductivity or varying the pH of the solution). The operating cost using EF process is obtained from the following equations [26, 27]:

Electrode consumption ( $C_{\text{electrode}}$ , kg/m<sup>3</sup>: kg of electrode dissolved/m<sup>3</sup> of effluent):

$$C_{\text{electrode}} = I \times RT \times M/n \times F \times V.$$

Electrical energy consumption ( $C_{\text{energy}}$ , kW h/m<sup>3</sup>):

$$C_{\text{energy}} = U \times I \times RT / V.$$

Chemical consumption ( $C_{\text{chemicals}}$ , kg of chemical/m<sup>3</sup>):

$$C_{\text{chemicals}} = \text{Chemicals used} / \text{m of effluent}.$$

$$\text{Operating cost (cost /m}^3) = aC_{\text{electrode}} + bC_{\text{energy}} + cC_{\text{chemicals}}.$$

Where  $I$  = electrical current (A),  $U$  = voltage (V),  $RT$  = treatment time (s),  $M$  = molecular mass of Al,  $Z$  = amount of electron moles (3 for Al),  $F$  = Faraday's constant (96,500 c/Mol),  $V$  = volume of wastewater (L),  $a$  = cost of aluminum (US\$/kg),  $b$  = electricity costs (US\$/kWh), and  $c$  = cost of chemicals which can be added (US\$/kg).

The electrical energy consumption "E" was about 1.38Kwh/m<sup>3</sup>. The operating cost (cost/m<sup>3</sup>) was about 0.3US\$/m<sup>3</sup>. Removal of bacteria, viruses, microorganisms, algae, etc. from the produced water is necessary to prevent scaling and water contamination. The residual microorganisms occurred naturally in the produced water may be removed (disinfect) using other effective technologies, such as Ultra Violet light treatment, chlorine or iodine reaction, ozone treatment and pH reduction [3].

These results reveal that the designed cell gave excellent results compared to previous studies as obtained by Tao Zheng [28]. The treatment of oil field alkali-surfactant-polymer-flooding produced water by using an Fe electrode showed that under the optimal conditions of current density of  $35\text{mA}/\text{cm}^2$ , pulse frequency of  $3.0\text{kHz}$ , electrode distance of  $1.0\text{cm}$ , and reaction time of  $40\text{min}$ , the removal efficiencies of chemical oxygen demand (COD), oils and greases, turbidity, total suspended solids, and polyacrylamide reach 98.3, 99.0, 98.8, 98.1 and 94.3%, respectively, with an energy consumption of  $0.19\text{kWh}/\text{kg COD}_{\text{removed}}$  and an electrode consumption of  $3.1\text{ kg Fe}/\text{kg COD}_{\text{removed}}$  [28].

#### 4. Conclusions

The pH is an important factor for removal efficiency of different pollutants. The maximum removal for all types of pollutants is achieved at pH6. It may be due to the stability of  $\text{Al}(\text{OH})_3$  which is soluble at high and low pH. The removal efficiency increased from about 38% to more than 96% with increasing current density from  $16$  to  $80\text{A}/\text{m}^2$ , at feed rate of  $60\text{ml}/\text{min}$  and pH7. This may be due to increasing the rate of electrochemical reactions, coagulant concentration produced, destabilized pollutant species and formation of small bubbles, which induced flotation. At pH7, feed flow rate of  $60\text{ml}/\text{min}$  ( $3.6\text{l}/\text{hr}$ ), current density of  $80\text{A}/\text{m}^2$  (1 Ampere) and Voltage 5 at  $25^\circ\text{C}$ , the removal efficiency of different constituents was range between 87.5 – 99.5%. The electrical energy consumption "E" was about  $1.38\text{Kwh}/\text{m}^3$ . The operating cost ( $\text{cost}/\text{m}^3$ ) was about  $0.3\text{US}\$/\text{m}^3$ . The treated water may be further disinfect using other the effective technologies such as Ultra Violet light treatment, chorine or iodine reaction or ozone treatment to remove residual bacteria, viruses, microorganisms, algae, etc.

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